

Daily Variation in Chemical Characteristics of Urban Ultrafine Aerosols and Inference of Their Sources

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A summer air quality monitoring campaign focusing on daily variation of ultrafine (<180 nm in diameter) particle chemical characteristics was conducted in a typical urban site in Los Angeles during June–July 2006. Ultrafine particles (UFP) were collected weekly for two 3 h periods each day, one to capture the morning commute (06:00–09:00 PDT) (Pacific Daylight Time) and one to investigate photochemically altered particles (13:00–16:00 PDT). Samples were analyzed for ionic compounds, metals, trace elements, elemental carbon, and organic carbon. In addition, measurements of individual organic species and their variation with time of day at the urban site were conducted. The relative abundances of alkanes, PAH, and hopanes in the morning denote a strong influence of commute traffic emissions on ultrafine particle concentrations. By contrast, afternoon concentrations of oxygenated organic acids and sulfate rose, while other species were diluted by increased mixing height or lost due to increasing temperature. These are clear indicators that secondary photochemical reactions are a major formation mechanism of ultrafine aerosols in the afternoon. The concentrations of organic species originating from vehicular emissions measured in this study compare favorably to those from freeway-adjacent measurements by using CO₂ concentrations to adjust for dilution, demonstrating the effectiveness of this tool for relating sites affected by vehicular emissions.

Introduction

Increasing epidemiological and toxicological evidence associates adverse human health effects with exposure to atmospheric ultrafine particles (UFP). Several studies have demonstrated the ability of ultrafine particles to induce oxidative stress and inflammation in cells, which may contribute to cardiovascular diseases (1). The inherent large surface area-to-mass ratio of UFP may result in increased

adsorption of organic molecules and the induction of oxygen radicals (2). Ambient UFP in urban areas originate from both primary sources (3) and secondary formation mechanisms (4), which can substantially change particle size and chemical composition as they evolve in the atmosphere (5) as well as directly produce new UFP (6).

Several studies have addressed ambient UFP chemical composition. Sardar et al. (7) measured UFP mass concentration of 4–5 μgm^{-3} at a major freeway site in downtown Los Angeles, with 70% of organic matter, 10% elemental carbon, 10–15% of sulfate and trace metals, and negligible nitrate. An organic tracer study at this same site using time-resolved data showed that hopanes—tracers for motor vehicle exhaust—were found mostly in the ultrafine (UFP) mode, and evidence for secondary organic aerosol production was found mostly in larger, accumulation mode particles (8). These observations were similar to those reported by Cass et al. (5) over a slightly different size range also in summertime Los Angeles. In addition to these generalized measurements of UFP composition, only a few studies have investigated the detailed UFP composition in the atmosphere (8).

In the present paper, we focus on the chemical composition of UFP in a typical urban site in Los Angeles near the downtown area. The evolution of carbonaceous compounds and various organics species from morning to afternoon has been measured to investigate the contributions of primary emissions and secondary photochemical reactions. A comparison of measured concentrations of polycyclic aromatic hydrocarbons (PAH) and hopanes/steranes between two sites: a nearby freeway (CA-110) and an urban location (current sampling site) was carried out by applying dilution ratios based on CO₂ concentrations (9). Additionally, an inorganic ion balance was used to investigate the acidity of ultrafine particles during the morning and afternoon periods. The present paper will provide insight into short-term variation of UFP chemical properties due to changes in source strength as well as atmospheric conditions.

Experimental Method

Sampling location. The present study took place between June 28 and July 27, 2006 over 4 consecutive weeks with sampling conducted only on weekdays. The sampling site was located at the Particle Instrumentation Unit (PIU) of the Southern California Particle Center and Supersite (SCPCS) near the University Park campus of the University of Southern California near downtown Los Angeles, CA. The PIU is within 150 m of a major freeway (Interstate-CA-110) and adjacent to a six level parking structure and various construction sites. An instrumented trailer is maintained inside PIU, and the aerosol sampling inlets were located at an elevation of ca. 4 m fixed on top of the trailer and within ca. 3 m horizontally of each other. Previous studies carried out in the same sampling site have described it as being affected by a typical mixture of urban pollution sources, including motor vehicle traffic (7).

Sampling Protocol. Aerosol sampling was accomplished by deploying two filter-based techniques: a custom-built high volume sampler (10) and Micro-Orifice Uniform Deposit Impactors (MOUDI, MSP, Inc., Minneapolis, MN). The high volume sampler has a nominal flow rate of 450 L min⁻¹ and separates particles into coarse ($D_p > 2.5 \mu\text{m}$), accumulation ($0.18 < D_p < 2.5 \mu\text{m}$), and ultrafine ($D_p < 0.18 \mu\text{m}$) modes. Accumulation mode aerosols were collected on quartz-fiber impaction strips (cut from Pallflex Tissuquartz 2500QAT-UP-8 \times 10, Pall Corp., East Hills, NY), and ultrafine aerosols were collected on TFE-coated glass fiber filters (Pallflex

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Fiberfilm T60A20-8 × 10, Pall Corp., East Hills, NY) seated in a specially designed 20 × 25 cm high-volume filter holder. The coated filters have been used to minimize organic vapor adsorption artifacts associated with quartz-fiber filters (8, 11). Parallel to the high volume sampler, two MOUDI's sampled concurrently at 30 Lpm to collect size-segregated particles in the accumulation mode ($0.18 < D_p < 2.5 \mu\text{m}$) and ultrafine mode ($D_p < 0.18 \mu\text{m}$). PTFE and quartz 37 mm filters were used as impaction substrates to collect ultrafine particles, whereas PTFE filters and Aluminum 47 mm substrates were used to collect accumulation mode particles in the two MOUDI's. Quartz and aluminum substrates were prebaked at 550 °C for 8 h, and TFE-coated glass fiber filters were precleaned with a solvent mixture as described by Fine et al. (8). All were stored in baked aluminum-foil-lined containers prior to sampling.

Composited aerosol samples were collected in the "Morning" (6:00–9:00 PDT) and "Afternoon" (13:00–16:00 PDT) periods over the 5 days of each sampling week for four consecutive weeks. Each weekly sample encompassed 15 h (5 days multiplied by 3 h per day) sampling for respective time periods. "Morning" period corresponds to rush hour traffic times when the ambient aerosols in the sampling site are dominated by particles freshly emitted from vehicles on the nearby freeway. "Afternoon" period represents the mixture of primary particles from traffic and secondary particles undergoing physical and chemical changes (i.e., photochemistry and possible volatilization if they contain labile species) during the day. Although the present study mainly focuses on UFP properties; to put the data into perspective, accumulation mode particles were also collected in the last week of sampling. All filters were sealed in annealed, foil-lined Petri dishes and stored in a freezer between sampling intervals.

Sample Analysis. Chemical composition and organic speciation analysis methods of the samples are presented in Supporting Information (SI).

Results and Discussion

Mass Concentration and Mass Balance. Throughout the entire campaign the meteorological conditions at the sampling site were typical of Southern California summer, with stable wind speeds at $1.64 \pm 0.74 \text{ m/s}$ and wind direction of 223 ± 28 degrees, which placed the sampling site directly downwind of the nearby freeway (and at ~150 m). The distance to the sampling site from the freeway is sufficiently long to place it outside the immediate "zone of influence" of the freeway, based on our previous work in Southern California (12, 13). Temperature and relative humidity showed strong diurnal profiles with higher temperature and lower humidity in the afternoon. Elevated afternoon ambient ozone concentrations further support enhanced photochemical activity during afternoons of this study. Detailed average and standard deviation of meteorological parameters and associated gases concentrations in the morning and afternoon periods are described in Table 1.

Weekly and average UFP mass concentrations as well as measured species concentrations in the morning and afternoon periods are shown in Figure 1. Mass concentrations of ultrafine particles (UFP, in the context of this paper defined as $\text{PM}_{0.18}$) ranged from 2.63 to $7.26 \mu\text{g}/\text{m}^3$ with an average value of $4.35 \pm 0.22 \mu\text{g}/\text{m}^3$ in the morning and $4.95 \pm 0.26 \mu\text{g}/\text{m}^3$ in the afternoon. Average UFP concentration is slightly higher (14%) in the afternoon than morning, which may suggest secondary aerosol formation and growth by condensation of low-volatility atmospheric oxidation reaction products onto pre-existing particles (14).

Chemical mass balance results show very good agreement between the reconstructed mass by summing the measured chemical species concentrations and the gravimetrically

TABLE 1. Meteorological Parameters and Measured Gases Concentrations in the Morning and Afternoon Periods during the Study

meteorological parameters	morning ^a	afternoon ^a
temperature (°C)	25 ± 3	38 ± 3
humidity (%)	70 ± 10	35 ± 7
wind speed (m/s)	0.96 ± 0.28	2.32 ± 0.29
wind direction (degree)	213 ± 35	233 ± 15

gas species		
CO (ppm)	0.75 ± 0.34	0.22 ± 0.09
NO ₂ (ppb)	38.4 ± 14.7	17.8 ± 4.2
NO _x (ppb)	95.4 ± 46.9	17.8 ± 4.7
O ₃ (ppb)	5.6 ± 5.8	57.3 ± 21.6

^a Presented data are the average and standard deviation during the time period.

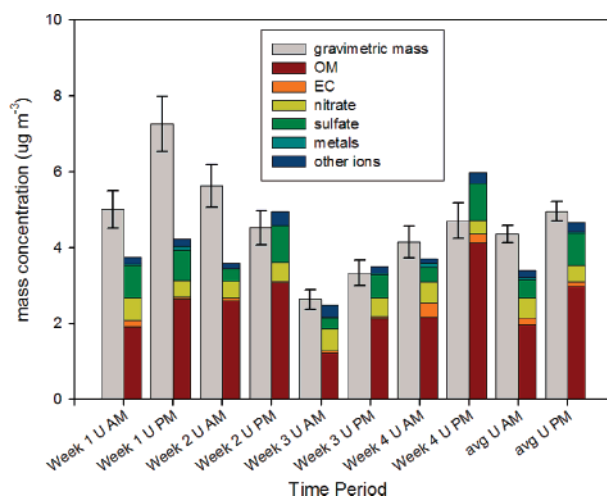


FIGURE 1. Weekly and average mass concentrations of ultrafine (U) particles and mass balance of measured species in the morning (AM) and afternoon (PM).

determined mass concentration. Conversion factors of 1.4 and 1.8 have been applied for the measured organic carbon concentrations in the morning and afternoon, respectively. A detailed discussion is described in Supporting Information. On average $78 \pm 14\%$ and $94 \pm 29\%$ of UFP mass can be explained by the measured chemical constituents in the morning and afternoon periods, respectively. The discrepancies in chemical versus gravimetric mass is likely caused by measurement uncertainty and particle-bound water.

UFP chemical composition varied to a slight extent during the study, with 50–73% OM, 1–11% EC, 6–23% nitrate and 9–23% sulfate. Similar chemical composition of UFP has been reported by Sardar et al. (7) and Cass et al. (5) in Southern California. Other reported ions include ammonium, sodium, potassium, chlorine, and phosphate. Average contribution of nitrate to UFP mass decreased from 16 to 10% due to its volatilization from particle-to-gas phase as temperature increases in the afternoon (15). EC fraction decreased from 5 to 2%, suggesting the decline of freeway traffic volume from morning to afternoon combined with the increase in mixing height of the atmosphere during that time. However, OM and sulfate contributions to UFP increased from 59 to 65% and 14 to 18%, respectively, indicating elevated secondary aerosol formation when higher photochemical activity occurs in the afternoon (16). Detailed chemical composition data will be further discussed in the subsequent sections.

Inorganic Ions. Figure 2 presents the ratio of sulfate, nitrate, and ammonium concentrations to the total UFP mass

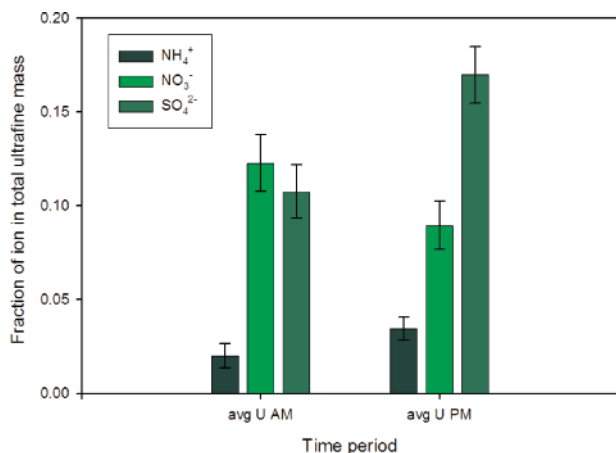


FIGURE 2. Mass fractions of sulfate, nitrate and ammonium in total mass of ultrafine (U) particles in the morning (AM) and afternoon (PM) periods.

concentrations of UFP in morning and afternoon periods. The measured average UFP sulfate concentrations were $0.47 \mu\text{g}/\text{m}^3$ and $0.84 \mu\text{g}/\text{m}^3$ in the morning and afternoon, respectively. Similar concentrations have been observed by Sardar et al. (7) in Los Angeles. Sulfate concentrations and mass fraction for both UFP and accumulation mode particles increased in the afternoon due to the photochemical origin by condensation of gaseous sulfuric acid from the oxidation of sulfur oxide gases (17). Average UFP nitrate concentrations were $0.53 \mu\text{g}/\text{m}^3$ and $0.44 \mu\text{g}/\text{m}^3$ in morning and afternoon, respectively. The decrease of nitrate concentrations in the afternoon reflects the increase in its dissociation constant with increasing temperature and decreasing relative humidity (18). The most abundant cation was ammonium, with average concentrations of 0.09 and $0.17 \mu\text{g}/\text{m}^3$ in morning and afternoon, respectively. The increase in ammonium by nearly the same percentage as sulfate from morning to afternoon indicates that a small amount of the photochemically produced sulfuric acid aerosol is neutralized by ammonia. The measured ion concentrations for UFP and accumulation mode particles allowed us to determine the degree to which particles in these two ranges are acidic or fully neutralized. Following the approach of Zhang et al. (19), particle acidity was examined on the basis of measured ammonium concentrations versus the concentration needed to fully neutralize the measured sulfate and nitrate. A value of unity suggests that sulfate and nitrate might be fully neutralized by ammonium in the form of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 . A value close to zero suggests that the particles are predominately H_2SO_4 . Figure 3 presents the ammonium ratio plots for weekly and average UFP and accumulation mode particles in the morning and afternoon. Accumulation mode PM are fully neutralized in both morning and afternoon periods, with the measured to the required for neutralization ammonium concentrations being very close to 1. On the other hand, UFP appear to be highly acidic during both sampling periods, with ammonium ratios of $0.29 (\pm 0.09)$ and $0.36 (\pm 0.14)$ in the morning and afternoon periods, respectively. The UFP acidity in the afternoon period is consistent with the findings of Zhang et al. (19) in Pittsburgh showing that ultrafine particles are acidic during the initial stage of the photochemically induced nucleation. The UFP acidity during the morning traffic period corroborates previous findings of studies characterizing vehicle emissions, showing that the UFP sulfate in vehicle exhaust is mostly in the form of sulfuric acid or ammonium bisulfate rather than ammonium sulfate (20). Previous investigators argued that UFP may be acidic in the immediate vicinity of the roadway, but they would become neutralized a short distance downwind since the reaction rate of ammonia with sulfuric acid particles is close

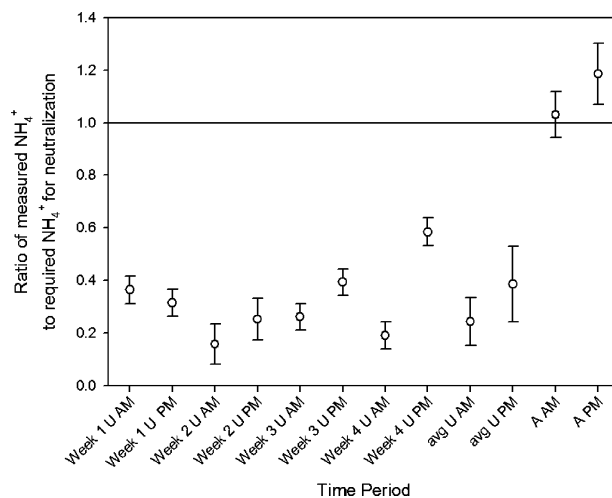


FIGURE 3. Weekly and average ratios of measured ammonium to required ammonium concentration for complete neutralization of ultrafine (U) and accumulation (A) particles in the morning (AM) and afternoon (PM) periods.

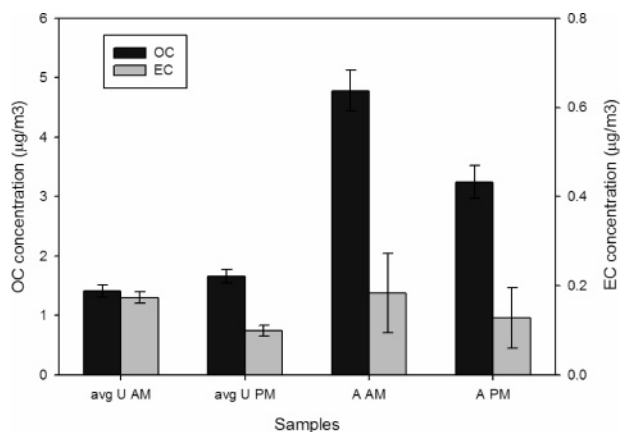


FIGURE 4. Average OC and EC concentrations of ultrafine (U) and accumulation (A) particles in the morning (AM) and afternoon (PM).

to collision-controlled (21) under excess ammonia conditions. A possible explanation for the observations in our site is that ammonia preferentially reacts with accumulation mode particles and is used up before it can react with UFP. Two mechanisms for this result may be that ammonia cannot access the sulfuric acid because of organic coatings on the sulfate core, and sulfate could be chemically interacting with EC. While both of these may inhibit the neutralization of sulfuric acid with ammonia, it must be stressed that no definite mechanism is currently known. In turn, the accumulation mode appears to be fully neutralized during both periods (Figure 3), a result that is also consistent with the fact that particles in that range represent an aged aerosol whose residence time in the atmosphere has been sufficiently long for it to be fully neutralized.

Carbonaceous Compounds. Figure 4 presents the average concentrations of organic carbon (OC) and elemental carbon (EC) measured in ultrafine and accumulation mode particles in morning and afternoon. The concentrations for UFP are the average of four weekly samples, and uncertainties were determined by the combination of weekly variation of sample concentrations and analysis error. Accumulation mode data were collected for one week and are presented here for comparison purposes.

The EC concentration of UFP decreased from $0.17 \mu\text{g}/\text{m}^3$ in the morning to $0.10 \mu\text{g}/\text{m}^3$ in the afternoon. The same trend was also found in the accumulation mode particles

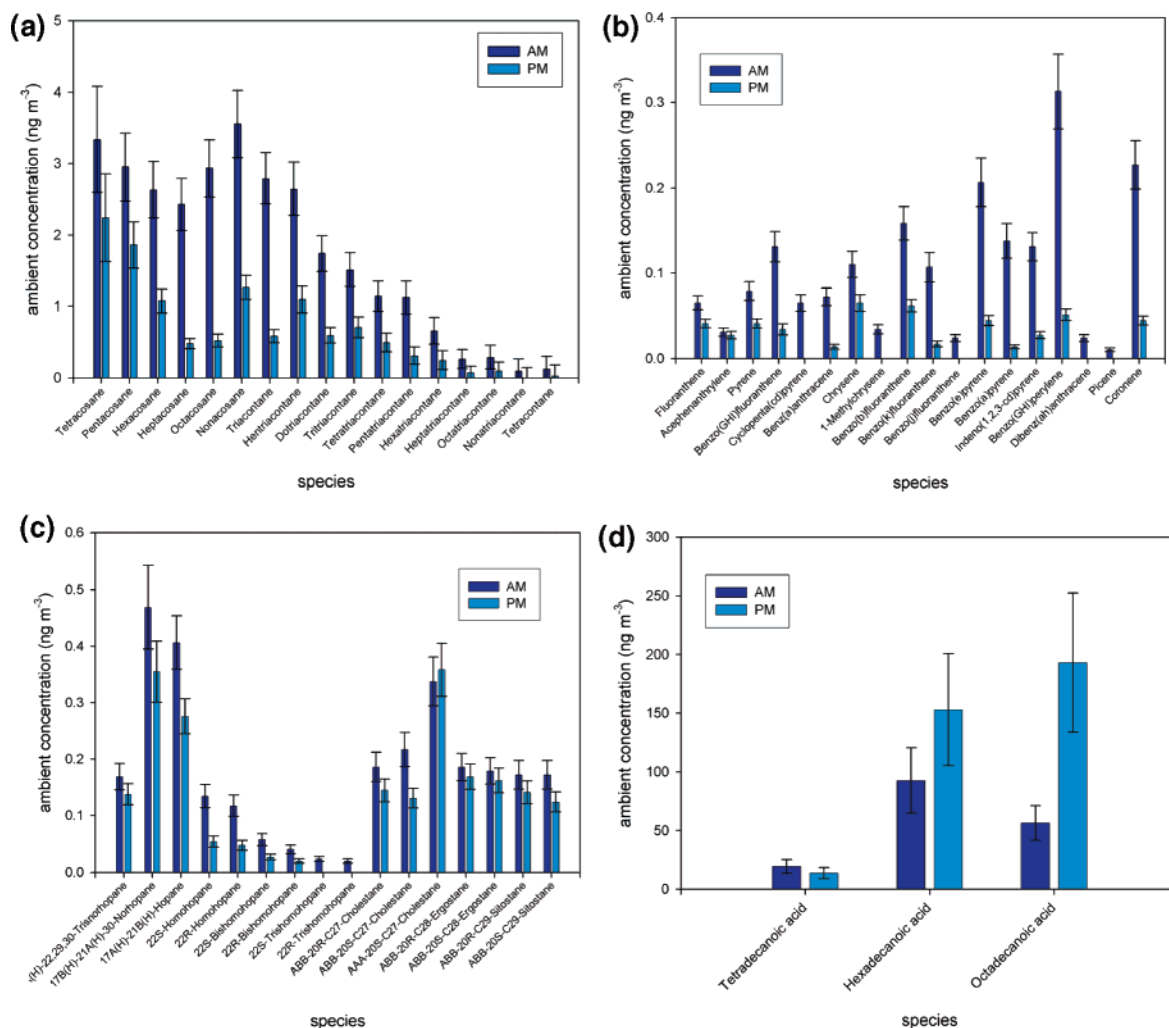


FIGURE 5. Average organic species concentration of ultrafine particles in the morning and afternoon: (a) *n*-alkanes; (b) PAHs; (c) hopanes and steranes; (d) organic acids.

with $0.18 \mu\text{g}/\text{m}^3$ in the morning and $0.13 \mu\text{g}/\text{m}^3$ in the afternoon. Traffic emissions are the predominant source of elemental carbon to the atmosphere in Los Angeles (22). In turn, higher EC concentration in the morning reflects higher traffic volume on the nearby 110 freeway during the morning sampling period. Decreased traffic and increased mixing height likely result in declining EC concentration in the afternoon. Similar observations have been found by Bae et al. (23) and Sardar et al. (7, 23).

In contrast to UFP EC, average UFP OC concentrations increased from $1.41 \mu\text{g}/\text{m}^3$ to $1.66 \mu\text{g}/\text{m}^3$ from morning to afternoon, which suggests that EC and OC do not share the same sources in the afternoon. While vehicular traffic is responsible for a portion of EC and OC at the site, elevated photochemical activity augments OC concentration in the afternoon. Interestingly, accumulation PM mode OC concentration decreased from 4.78 to $3.24 \mu\text{g}/\text{m}^3$ in the afternoon, as shown in the figure. Decreasing accumulation mode OC concentrations are likely the result of a regional OC concentration being diluted as mixing height increases in the afternoon.

Organic Speciation. *n*-Alkanes. The average mass concentrations of C_{24} – C_{40} *n*-alkanes during the campaign are presented in Figure 5(a) and tabulated in Table S2 (SI). Sums of weekly averaged average *n*-alkanes (C_{24} – C_{40}) concentrations of ultrafine particles were 30.2 and $11.7 \text{ ng}/\text{m}^3$ in the morning and afternoon, respectively. Carbon preference index (CPI) can be used to determine the anthropogenic and

biogenic sources of *n*-alkanes. It is defined as the sum of the concentrations of the odd carbon number alkanes divided by that of the even carbon number alkanes (24). Previous studies have shown that *n*-alkanes attributed to anthropogenic emission (e.g., gasoline residues) have CPIs close to 1. In rural areas, CPIs are generally higher than 2.0 due to biogenic influence (24). In the present study, CPIs of UFP *n*-alkanes are 1.1 and 1.0 in the morning and afternoon, respectively, indicating the strong influence of vehicular emissions to the sampling site during the campaign. As shown in the figure, the measured C_{24} – C_{40} *n*-alkanes species showed much higher concentrations in the morning, which can be explained by the strong source strength of vehicle exhaust from morning commute traffic. The drop in their concentrations in the afternoon may be due to the combined effects of decrease in traffic volume, increase in atmospheric mixing height, and possible loss due to volatilization of some of these species, which results in gas-particle partitioning back into the gas phase and recondensation onto larger particles when temperature increases (25, 26).

Polycyclic Aromatic Hydrocarbons (PAH). In the present study, 18 polycyclic aromatic hydrocarbons (PAH) have been identified and quantified in UFP. Figure 5(b) and Table S3 (SI) present the average mass concentrations of different PAH species during the campaign. Sums of weekly average PAH concentrations were 1.93 and $0.49 \text{ ng}/\text{m}^3$ in morning and afternoon, respectively. PAH are semivolatile organic compounds existing in both gas and particle phases, and

their concentrations in the atmosphere depend on various factors such as source strength, meteorological conditions, gas-particle partitioning, and wet/dry deposition (27). PAH may come from both anthropogenic sources and natural processes, but the former dominate urban areas (28). The nearby freeway is the only documented source of PAH at the USC sampling site (<http://www.arb.ca.gov/ch/chapis1/chapis1.htm>). As shown in the figure, concentrations of PAH are higher in the morning period when the nearby freeway is congested with vehicles during the morning commute. As in the case of *n*-alkanes, the decrease in PAH concentration in the afternoon reflects the combined effects of reduction in traffic, increase in mixing height, and also possible volatilization, especially of the lower molecular weight PAH, when temperature rises in the afternoon (29). Additionally, several studies, including Grosjean et al. (30) and Arey et al. (31), have reported reactions of PAH with oxidizing gases (ozone, nitrogen oxides, hydrogen peroxide, etc.), which may also contribute to the lower levels of these species in the afternoon. Both roadway tunnel studies (32, 33) and dynamometer studies (34, 35) have found that diesel vehicle emissions are enriched in lower molecular weight PAH (e.g., alkylated phenanthrenes, chrysene), whereas higher molecular weight PAH are associated with gasoline vehicle emission (e.g., benzo (ghi) perylene, coronene). The lower concentrations of PAH with molecular weight <228 compared to heavier molecular weight PAH are therefore consistent with the predominantly gasoline-vehicle traffic in the nearby CA-110 freeway (roughly 95–97%) (Caltrans- www.dot.ca.gov), as shown in the figure.

Hopanes and Steranes. Sixteen hopanes and steranes in the UFP range have been identified and quantified in the present study. Sums of weekly average hopanes and steranes concentrations were 2.89 and 2.15 ng/m³ in morning and afternoon, respectively. Figure 5(c) and Table S4 (SI) show the average mass concentrations of the individual species in the morning and afternoon. Hopanes and steranes are found in lubricant oils used by both diesel and gasoline vehicles (22), so they have been used as organic tracers of particles emitted from motor vehicles (36). Similarly to alkanes and PAH, the majority of the hopanes and steranes exhibited lower concentrations in the afternoon with a decline by an average of 26%, compared to 61% for alkanes and 75% for PAH. These diurnal changes of concentrations reflect the combined changes in source strength and mixing height. The larger differences in alkanes and PAH may be due to their higher volatility compared to hopanes and steranes, which increases their partitioning from the PM to the gaseous phase as the temperature rises in the afternoon.

Organic Acids. A total of 31 organic acids in UFP were identified in the present study. Sums of weekly average concentrations of *n*-alkanoic acids between C₁₄ and C₃₀ in UFP are 182.0 and 372.1 ng/m³ in morning and afternoon, respectively. Octadecanoic acid (C₁₈) was the most abundant species, followed by hexadecanoic acid (C₁₆) and tetradecanoic acid (C₁₄), with significantly lower concentrations of other acid species. The results are consistent with observations in other locations by Park et al. (37) and Simoneit (24) for fine particles. Figure 5(d) presents the average mass concentrations of the three most abundant acid species in morning and afternoon, and the rest of the organic acids are presented in Table S5 (SI). As shown in the figure, hexadecanoic acid and octadecanoic acid have much higher concentrations in the afternoon, resulting from photochemical formation (16). However, tetradecanoic acid showed slightly lower concentration in the afternoon which may be explained by its partitioning in the gas phase in the afternoon due to its higher volatility than C₁₆ and C₁₈ acids. Although other measured organic acids have very low concentrations in UFP, there is a discernible increase in concentrations from

morning to afternoon. The most likely explanation for the increase of these species observed in the afternoon is that they are products of secondary photo-oxidation of either organic gases and/or semivolatile species evaporating from primary particles (16). Food cooking is a source of some organic acids, but Rogge et al. (38) argued that atmospheric chemistry is more likely responsible for their formation because food cooking alone cannot explain the entire mass of these compounds typically measured in the atmosphere. In a recent article on the origin of the secondary organic aerosol, Robinson et al. (39) demonstrates how photooxidation of low volatility gas-phase species evaporating from primary particles emitted by vehicles rapidly generates organic aerosols, thereby greatly exceeding the contribution from known secondary organic aerosol precursors.

Comparison of Organic Speciation at the Urban Site with Measurements at the CA-110 Freeway. The observed diurnal variation of UFP chemical composition at USC from morning to afternoon reflects mostly the impact of vehicular emissions from the nearby freeway (CA-110). To further investigate the impact of dilution on UFP organic species, Figure 6(a) and (b) display comparisons of UFP concentrations of hopanes–steranes and PAH measured at USC to those measured next to the CA-110 freeway (40). These measurements were conducted within 5 meters of CA-110, a gasoline-only stretch of highway between downtown Los Angeles and Pasadena, California, during the summer of 2004. Samples were collected between 12:00 and 17:00 PDT from Monday to Friday, which more closely resembles the afternoon sampling period of the current study. Thus, for consistency, only the afternoon USC data were compared to the CA-110 data.

Studies have shown that atmospheric dilution has a large effect on particle number concentrations with increasing distance from a freeway (13). It is important to correct for the dilution ratio in various sampling locations to decouple the effects of fleet operation and ambient conditions on particle concentrations from the influence of specific sampling location (9). The dilution ratio is calculated as the fleet-average exhaust CO₂ concentration over the incremental ambient CO₂ increase (in the range of 470–480 ppm) as described by our recent work (9). A comparison of dilution ratios from the CA 110-freeway site to the USC site yielded a dilution factor of 4.4–8.8 between the CA-110 freeway and the site at USC, based on ambient afternoon CO₂ concentrations between 390 and 400 ppm at USC and assuming a CO₂ background concentration of 375 ppm. This ratio is similar to that reported by Marshall et al. (41), citing in-vehicle concentrations of carbon monoxide (another tracer of atmospheric dilution) being about 4–5 times greater than those of a typical ambient urban site.

Figure 6(a) presents the comparison of hopanes and steranes concentrations measured at the 110 freeway and in the present study. The y-axes are offset by a factor of 5 to account for the difference in dilution ratios between the two sites. The majority of the hopanes species concentrations measured in the proximity of the freeway closely match those at USC, adjusted for dilution, as shown in the figure, thus reinforcing the use of hopanes as conservative and reliable tracers of vehicular emissions (42). Steranes (except sitostane), however, showed higher ambient to freeway ratio compared with hopanes. The overall average CA-110 freeway to USC concentration ratio for hopanes and sitostane is 5.6, which is well within the dilution factor range calculated based on CO₂ concentrations.

Figure 6(b) presents the comparison of PAH concentrations measured adjacent to the CA-110 freeway to those at USC. As shown in the figure, the dilution-normalized concentrations compare favorably between sites, confirming the link between vehicular emissions and PAH. The average

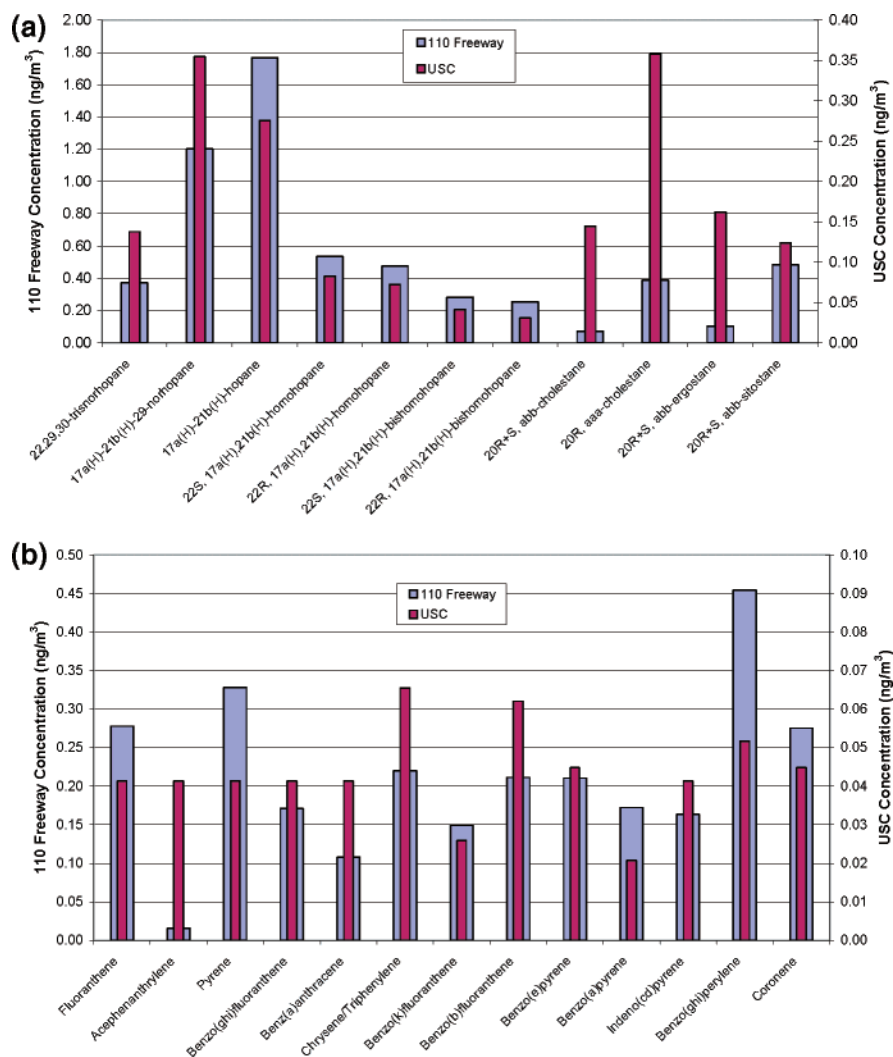


FIGURE 6. Comparison of measured organic tracers concentrations in 110 and USC applying dilution ratio: (a) hopanes and steranes; (b) PAH.

CA-110 freeway to USC ratio of PAH is 5.1, which is slightly lower than the hopane–sterane ratio of 5.6 based on pure atmospheric dilution, but still within the calculated range. It is interesting to note that, although these species are generally considered to be less conservative than hopanes/steranes, and thus are subject to physical and/or chemical transformation as they move from the source (freeway) to the USC sampling location, our data indicate that their decrease in concentration with distance from the freeway is mostly driven by atmospheric dilution. A possible explanation for this is the different vehicle mix at the USC site, having a relatively low fraction (4–5%) of diesel vehicles. Diesel vehicles are known to have higher emission factors than gasoline vehicles for nearly all organic species, but their emission factors are considerably higher for the more volatile, low molecular weight PAH (e.g., pyrene, benzo(ghi)fluoranthene, benz(a)anthracene) compared to more conservative species such as heavier PAH and hopanes/steranes (11).

Since this study is the first of its kind to report speciated organic carbon in UFP for both morning and afternoon periods at an urban site, more data are warranted to corroborate the results herein. Comparisons of measured organic acids within sites continue to reveal periods of high photochemical activity, whereas comparisons of dilution-adjusted primary-emitted compounds between sites can strengthen the link between source and receptor. Both techniques should be employed extensively in future attempts

to reconcile spatial and temporal variability of UFP and their sources.

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Supporting Information Available

Chemical composition and organic speciation analysis methods of the samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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